ON THE HYPOTHESIS OF CONSTANT ATOMIC RADII

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Introduction.—It has been suggested[1] that the data from the study of crystal structures are in agreement with an hypothesis which assigns to the atoms of each element a definite size and builds up crystals through their packing together. The structures of many more crystals have been determined since this hypothesis was first advanced and information has arisen from some of these which does not accord with the idea of constant atomic radii. For this reason, and also because various discussions of "shapes" of atoms based upon the assumption of its correctness have appeared, a reëxamination of the question in the light of the best data now available is required.

A knowledge of its precise status is also of importance to the crystal analyst because the agreement of such a simple hypothesis with results of experimentation would make possible the location of the atoms in crystals whose structures are far too complicated for complete study by existing X-ray methods.

The Calculation of Atomic Radii.—Calculation of the "sphere of influence" of atoms can now be made from four independent starting points: (1) from metals; (2) through the diamond and divalent metal carbonates of the calcite group; (3) from pyrite (FeS_2); (4) with the aid of cesium dichloro-iodide ($CsCl_2I$). If atomic radii are strictly constant all of these approaches should lead to the same result. It has been quite clear for some time, however, that the metals do not fit well into this scheme. Calcite and its related minerals likewise present difficulties because of the two different assignments of position which have been made to the oxygen atoms. The results from pyrite and cesium dichloro-iodide are

in substantial agreement and have therefore been chosen as offering the basis for the fairest test of this hypothesis. Of these last two cesium dichloro-iodide is the most practicable for use as a primary standard because crystals containing halogen atoms have been most studied while few sulfides have as yet been investigated. It is of course evident that the conclusiveness of the test of this hypothesis is not concerned with the precise absolute value of the atomic radii so long as conflicting standards are not used simultaneously. Consequently the conclusions which may be drawn from the work which follows would not be invalidated if the chlorine atom which will appear as primary standard were given a somewhat different size.

Starting from cesium dichloro-iodide the following procedure has been employed in calculating atomic radii. The distance along a trigonal axis from an atom of cesium through one of chlorine to an iodine atom is 6.102 Å. U. The nearest approach of cesium and iodine atoms in crystals of cesium iodide is 3.94 Å. U. The diameter of the chlorine atom may then be taken directly as the difference between these two distances or 2.162 Å. U. From this initial value radii are calculated for other atoms either from the most adequately studied compound available or, as in the case of the alkali halides, through an averaging of several of these values. The radii thus obtained for the electronegative atoms for which comparative data exist are as follows:

ATOM	"RADIUS"	ATOM	"RADIUS"	ATOM	"RADIUS".
H	0.55 Å. U.	Br	1.24[5] Å. U.	N	0.62[6] Å. U.
F	0.62[1]	I	1.50[1]	O	0.64
Cl	1.08[1]	(CN)	1.22	S	1.04[3]

Comparisons between calculated and observed interatomic distances which are, respectively, favorable to or in disagreement with the hypothesis of constant radii are collected in tables 1 and 2.

TABLE 1

DATA THAT ACCORD WITH AN HYPOTHESIS OF CONSTANT ATOMIC RADII

CRYSTAL	BETWEEN ATOMS	INTERATOMIC DISTANCES	
		CALCULATED	OBSERVED
Li	Li–Li	3.00Å. U.	3.03Å. U.
LiH	Li–H	(2.05)	2.05
LiF	Li–F	2.12	2.07; 2.01
LiCl	Li–Cl	2.581	2.585
LiBr	Li–Br	2.746	2.74
LiI	Li–I	3.00	3.03
NaF	Na–F	2.35	2.34; 2.305
NaCl	Na–Cl	(2.814)	2.814
NaBr	Na–Br	2.976	2.975; 3.01

NaI	Na–I	3.23	3.235; 3.25
NaNO₃	Na–O	2.37 (if u = ¹/₄)	2.388
KF	K–F	2.676	2.68; 2.69
KCl	K–Cl	3.136	3.13
KBr	K–Br	3.301	3.30
KI	K–I	3.556	3.55
KCN	K–(CN)	(3.27)	3.27
RbCl	Rb–Cl	3.30	3.30
RbBr	Rb–Br	3.466	3.465
RbI	Rb–I	3.72	3.68; 3.654
CsF	Cs–F	3.06	3.015
CsCl	Cs–Cl	3.52	3.568
CsBr	Cs–Br	3.686	3.724; 3.713
CsI	Cs–I	(3.94)	3.94; 3.966
MgO	Mg–O	(2.10)	2.10
Mg(OH)₂	Mg–O	2.10	2.09 (probably)
CaF₂	Ca–F	(2.368)	2.368
CaO	Ca–O	2.387	2.384
CaCO₃	Ca–O	2.387 (if u = ¹/₄)	2.372
BaO	Ba–O	(2.74)	2.74
BaF₂	Ba–F	2.72	2.684
ZnS	Zn–S	(2.337)	2.337
ZnO	Zn–O	1.934	1.942
Cu₂O	Cu–O	(1.845)	1.845
CuCl	Cu–Cl	2.286	2.377; 2.32
CuBr	Cu–Br	2.451	2.52; 2.49
CuI	Cu–I	2.706	2.64; 2.63
AgCl	Ag–Cl	2.725	2.78; 2.76
AgBr	Ag–Br	(2.89)	2.89
Ag₂MoO₄	Ag–O	2.284	2.315
CaCO₃	C–O	(1.245)	1.245 (if u = ¹/₄)
MnCO₃	C–O	1.245	1.275 (if u = 0.27)
Sn (gray)	Sn–Sn	2.734	2.798
K₂SnCl₆	Sn–Cl	(2.448)	2.448
(NH₄)₂SnCl₆	Sn–Cl	2.448	2.462
Ag₂MoO₄	Mo–O	(2.00)	2.00
Mo	Mo–Mo	2.72	2.72; 2.668
FeS₂	Fe–S	(2.254)	2.254
Fe	Fe–Fe	2.422	2.476
Fe₃O₄	Fe^{II}–O	1.851	1.797
MnS	Mn–S	(2.607)	2.607
MnCO₃	Mn–O	2.204	2.17 (if u = 0.27)
Mn(OH)₂	Mn–O	2.204	2.08–2.26 (2.19 is best)
K₂PtCl₄	Pt–Cl	(2.27)	2.27
(NH₄)₂PtCl₆	Pt–Cl	2.27	2.16–2.36
K₂PdCl₄	Pd–Cl	(2.29)	2.29
(NH₄)₂PdCl₄	Pd–Cl	2.29	2.34 (approximately)

NOTE.—The references for the crystal dimensions used in preparing this and the following table can be found in a recent paper by the writer (*J. Frank. Inst.*, Feb., 1923). The numbers enclosed in parentheses have been used directly in calculating values for "atomic radii."

TABLE 2

DATA DISAGREEING WITH AN HYPOTHESIS OF CONSTANT ATOMIC RADII

CRYSTAL	BETWEEN ATOMS	INTERATOMIC DISTANCES	
		CALCULATED	OBSERVED
Na	Na–Na	3.46 Å. U.	3.724 Å. U.
K	K–K	4.11	4.504
$K_2Zn(CN)_4$	K–(CN)	3.27	3.14
K_2PtCl_4	K–Cl	3.136	3.227
K_2PdCl_4	K–Cl	3.136	3.23
K_2SnCl_6	K–Cl	3.136	3.48
$CsCl_2I$	Cs–Cl	3.52	3.65
$CsCl_2I$	Cs–I	3.94	4.18
Be	Be–Be	(2.234)	2.234
BeO	Be–O	1.757	1.648 and 1.65 (if $u = \frac{5}{8}$)
Mg	Mg–Mg	2.92	3.22
Ca	Ca–Ca	3.494	3.926
Zn	Zn–Zn	2.588	2.93 (if $u = \frac{1}{2}$)
$K_2Zn(CN)_4$	Zn–(CN)	2.514	2.715
Cd	Cd–Cd	3.44	3.30 (if $u = \frac{1}{2}$)
CdO	Cd–O	(2.36)	2.36
$K_2Cd(CN)_4$	Cd–(CN)	2.94	2.80
CdI_2	Cd–I	3.22	2.98
Cu	Cu–Cu	2.41	2.542
Ag	Ag–Ag	3.288	2.866
Ag_2O	Ag–O	2.284	2.06; 2.04; 2.03
AgI	Ag–I	3.145	2.81 and 2.825
Diamond	C–C	1.21	1.542
Si	Si–Si	2.194	2.352
$(NH_4)_2SiF_6$	Si–F	(1.718)	1.718
$NaNO_3$	N–O	(1.266)	1.266
NH_4Cl	N–H–Cl	2.807 [3.34]	3.342
NH_4Br	N–H–Br	2.972 [3.507]	3.454
NH_4I	N–H–I	3.227 [3.76]	3.60
$NiCl_2.6NH_3$	N–H–Cl	2.807 [3.34]	3.56
$NiBr_2.6NH_3$	N–H–Br	2.972 [3.507]	3.70
$NiI_2.6NH_3$	N–H–I	3.227 [3.76]	3.89
$(NH_4)_2PdCl_4$	N–H–Cl	2.807 [3.34]	3.328
$(NH_4)_2PtCl_6$	N–H–Cl	2.807 [3.34]	3.48
$(NH_4)_2SnCl_6$	N–H–Cl	2.807 [3.34]	3.54
$N_2H_6Cl_2$	N–H–Cl	2.807	3.143
$CsCl_2I$	Cl–I	2.582	2.23–2.29 (if $u = 0.312$– 0.317)
CdI_2	I–I	3.00	4.206
Fe_3O_4	Fe^{III}–O	1.85	2.07
NiO	Ni–O	(2.085)	2.085
Ni	Ni–Ni	2.89	2.50
$NiCl_2.6NH_3$	Ni–NH	2.07 or 3.17	2.29–2.47
Pt	Pt–Pt	2.378	2.77; 2.838
Pd	Pd–Pd	2.418	2.788; 2.754

NOTE.—The second column under calculated distances (enclosed in brackets) gives distances which are calculated upon the assumption of a definite but large volume for the ammonium group.

The many examples of table 2 show clearly and conclusively that the simple hypothesis which assigns a definite size to each atom and builds up crystals by packing these atoms together is not in harmony with experiment.

The fact that such metals as zinc and cadmium crystallize with an axial ratio which is considerably removed from that corresponding to the closest packing of spheres might suggest[2] that the original hypothesis could be modified by assigning to each atom a definite shape. Atoms thus might have different atomic radii depending upon their orientation within the crystal. This sort of a modification fails to account, for example, for the increasing separation between alkali and halogen atoms in such complex halides as the chloroplatinites and chloroplatinates or for the observation that silver, which shows very different radii in silver chloride and silver iodide, nevertheless crystallizes in the cubic close packing of spheres.

From the little that is known of the complexities of atomic structure it would be most surprising to find an hypothesis of constant atomic radii, or any simple modification of it, in accord with experiment. It will, nevertheless, be noted that a rule of constant atomic radii appears to hold true within such large groups of isomorphous compounds composed of two kinds of atoms as those alkali halides which have the sodium chloride arrangement. This may be interpreted to mean that as long as the number and distribution of one kind of atom about the other remain the same, the interatomic distances are additive in passing from crystal to crystal. When the atomic arrangement is closely alike in two crystals the corresponding interatomic distances may also not be greatly different. Thus each silver atom in silver molybdate is surrounded, as in the sodium chloride arrangement, by six oxygen atoms and the distance from silver to oxygen is calculable from the interatomic distances in the sodium chloride-like silver chloride or bromide.

The experimental data show that whenever the atomic environment (meaning thereby the manner of arrangement of atoms of one kind about those of the other) is changed, the corresponding interatomic distances are also varied. It is to be anticipated that the exact manner of change of interatomic distances with atomic environment will be understood only when knowledge of atomic structure has so far progressed that a calculation of the stabilities of different atomic arrangements is possible. In the meantime some working rules of a qualitative nature may be developed; but the existing crystal structure data are not adequate to establish them.

Conclusion.—From the crystal structure data which are presented in table 2 it must be concluded that the hypothesis of constant atomic radii is not in agreement with existing information. These data, however, conform to the rule that in isomorphous crystals composed of only two

kinds of atoms the interatomic distances have additive properties which can be illustrated through a summing up of "atomic radii." The data also show that for compounds of different crystal structures in which the atomic environments are different the interatomic distances likewise are unlike. Where the changes of environment are relatively small this change in interatomic distance may be almost negligible; in other cases it amounts to several tenths of an Ångstrom unit.

[1] W. L. Bragg, London, *Phil. Mag.*, **40**, 1920 (169).

[2] For instance see W. P. Davey, *Physic. Rev.*, *Ithaca*, **19**, 1922 (248).

PHOTOGRAPHIC DETERMINATION OF PARALLAXES WITH THE 100-INCH REFLECTOR

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In the issue of these Proceedings for April, 1915, were communicated the first results of parallax determinations with the Mount Wilson 60-inch reflector. The work has progressed steadily until now over 170 objects have been measured. The probable errors as well as the systematic errors are small, viz., $\pm 0''.0056$ and $-0''.0024$. On account of the difficulty in guiding at the Cassegrain focus on stars of southern declination, only a very few of these objects were placed on the observing program. Moreover, for several very faint stars and for stars in extremely poor fields it became necessary either to increase the exposure-time, which as a rule was fifteen minutes, or to use another instrument. A trial was accordingly made with the Newtonian arrangement of the 100-inch Hooker telescope (focal length 42 feet).

For four fields the plates have now been measured and reduced; the results are as follows:

OBJECT	PG. MAG.	α 1900 H. M. S.	δ 1900	π REL.	P. E.
Wolf 1037	14.5	22 23 44	$+ 5° 20'$	$+0''054$	$\pm 0''004$
Wolf 1039	13.8	23 29 2	$- 0° 21'$	$+0.056$	0.004
Wolf 1040	14.5	23 31 37	$+ 0° 37'$	$+0.057$	0.007
N.G.C. 7293	13.3	22 24 18	$-21° 21'$	$+0.058$	± 0.005

The first three stars have very large proper motions, which according to Wolf are $1''.57$, $1''.44$ and $1''.23$ annually. From the parallaxes derived here, they appear to be stars of very faint absolute magnitude, about $+13$